

Structure of dense amorphous carbon studied by EXAFS

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INTRODUCTION

Previous experiments¹ studied the bonding structure of dense amorphous carbon (a-C) films by analyzing their NEXAFS spectra using the *building block* model². This model considers that NEXAFS spectroscopy probes the final-state wave function near the excited atom. This means that the NEXAFS spectrum of a complex carbon structure should be equivalent to the sum of the NEXAFS spectra of their most simple units. Each of these simple units are differentiated in the spectra because the position in energy of the σ^* resonance depends on the conjugation state of the bond and the bond length². This is particularly interesting in a-C since it is supposed to be a mixture of atoms either sp^3 or sp^2 hybridized, i.e., forming single and double bonds with the consequent variations in bond length and bond conjugation. The analysis of the NEXAFS spectra of a-C should allow then to know the kind of carbon bonds present in the material, estimate their bond lengths and even quantify their relative proportion. Such an analysis in a dense a-C film yielded a relative intensity of the σ^* resonance for sp^3 bonded atoms that was lower than expected, only 20% of the total intensity for the σ^* band, when the sp^3 proportion deduced from the π^* to σ^* ratio was about 60%¹. In addition to this, the most intense peak assigned to sp^3 bonded atoms was shifted to lower photon energies than expected if the bond was related to diamond. This σ^* component was found at 288.5 eV, suggesting that those atoms had bond lengths longer than in diamond, of about 0.157nm instead of 0.154nm. The present EXAFS study tries to validate this method for the analysis of the NEXAFS spectra, i.e., to check if the estimated bond lengths from NEXAFS are similar to the obtained from EXAFS, and what is the truly proportion between sp^2 and sp^3 bonded atoms, since the amplitude of the EXAFS oscillations depends only on the coordination numbers and not in the kind of bonding.

EXPERIMENT

The samples were deposited from a cathodic arc plasma source in the Plasma Laboratory at the LBNL³. To avoid oxygen adsorption at the surface, the samples were transported after deposition to the analysis chamber in a low vacuum chamber (10^{-3} mbar). Nevertheless, oxygen contamination was found in the films, about 4%. EXAFS spectra were taken in the Materials Sciences beam line 9.3.2. Spectra were taken at liquid nitrogen temperature and after annealing at different temperatures up to 800° C. The intensity of the beam was taken from a piece of sputtered Si wafer, clean of carbon and oxygen.

EXAFS ANALYSIS: PRELIMINARY RESULTS

Despite the extremely low concentration of oxygen contamination found in the films, its x-ray absorption intensity was enough to “poison” the spectra. The O1s K edge is at 531eV, close to the third EXAFS oscillation from the C1s K edge. Although the amplitude of the EXAFS oscillations for oxygen were small, they were non-negligible compared to the amplitude of the C1s EXAFS oscillation at such photon energy. The C1s EXAFS oscillations were filtered from

the O1s EXAFS K edge bearing in mind that, at the O1s K edge energy, the period of the C1s EXAFS oscillations is much longer than the period for the O1s oscillations. The filtering was done using the AUTOBK⁴ code implemented in the IFEFFIT program created by M. Newville⁵. The resulting normalized EXAFS signal of a dense a-C film at RT, background removed and k^2 weighted, is shown in figure 1. The C-C phase shifts and scattering factors were obtained from the self-consistent calculations of FEFF8.10 code⁶. The best fit was obtained by combining single scattering paths with different scattering lengths. The resulting radial distribution function shown in figure 2 consist of a histogram made of 27 equidistant components or scattering paths⁷. The search for the best radial distribution was done starting from a low number of single scattering paths (initially only two), and progressively increasing the number of scattering paths, searching for the best solution at every step. The best solution for a given number of scattering paths was considered the initial guess at the next step, when the number of paths was increased. The comparison between the best solution and the module of the Fourier transformed EXAFS signal is compared in figure 3.

The radial distribution neatly distinguish as first neighbors two atom environments with distances similar to graphite and diamond, at 0.143nm and 0.157nm. Note that both distances, in particular the distance found for the diamond-like environment, is astonishingly similar to the estimated from the NEXAFS analysis. The area of the radial distribution at both distances is similar, indicating that the relative proportion of sp^2 hybridized atoms is about 50%. This fit fails in the calculation of the coordination numbers since the sum of the area under both distances should be lower than 4 and it is 4.8. This large number is probably due to the low number of oscillations that can be analyzed at the C1s K edge.

A surprising result that must be taken with care is the next-nearest neighbors shell that is shown in the radial distribution for distances longer than 0.16nm. Radial distribution functions of other dense a-C films obtained by electron and neutron scattering have never observed carbon atoms at such distances⁸. Next-nearest neighbors at such distances suggest very small bond angles compatible with a very strained structure and with the presence of three and four member carbon rings.

CONCLUSIONS

A preliminary EXAFS analysis of a dense a-C film yielded distances and environments compatible with the analysis of its NEXAFS spectrum using the *building block* model and the dependency of the σ^* resonance energy with bond length. The analysis showed the presence of atoms at distances between 0.16 and 0.21nm which were not observed previously by other scattering techniques. Analysis of the EXAFS spectra of the sample annealed at different temperatures and of another samples with a lower concentration of sp^3 bonded atoms would test the validity of the presented analysis.

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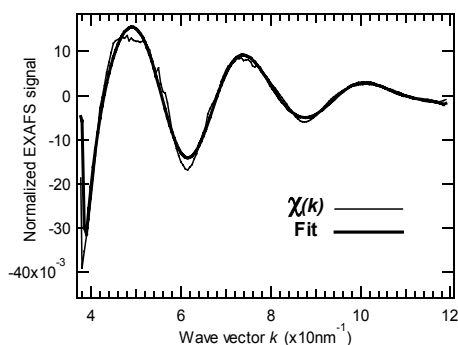


Figure 1. Normalized EXAFS signal, k^2 weighted, of a dense a-C film.

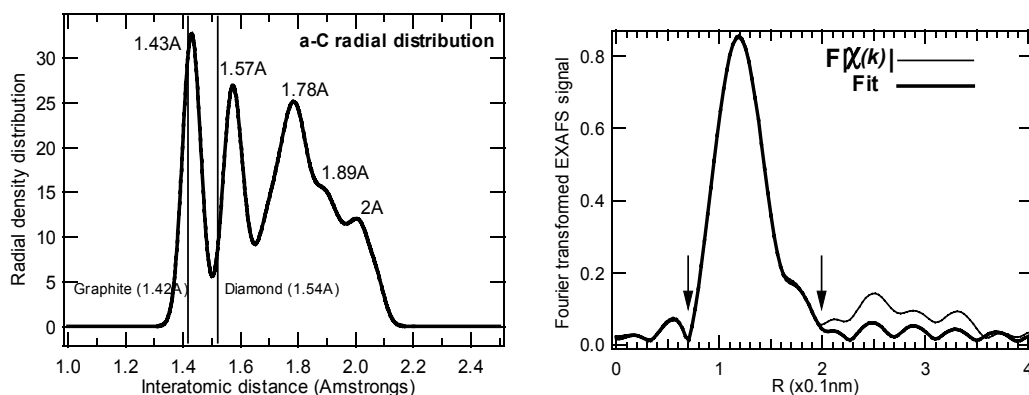


Figure 2. Radial density distribution function for a dense a-C film deduced from the analysis of its EXAFS spectrum taken at RT.

Figure 3. Module of the Fourier transformed EXAFS signal of a dense a-C film compared with the fit using the radial density distribution function shown in figure 2. Marked with arrows the fitted region.